19 FRENCH REPUBLIC

NATIONAL INSTITUTE
FOR INDUSTRIAL PROPERTY

PARIS

11 Publication No.:
(To be used only for classification and requests for copies)

2.105.539

21 National Registration No.:
(To be used for the payment of annual payments, requests for official copies and any other correspondence with the INPI)

70.32971

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PATENT OF INVENTION

FIRST AND SOLE PUBLICATION

[ALKYLPHENOL AMINOPROPYL ETHERS - PREFERABLY WITH ALKYLPHOSPHORIC ACIDS AS MULTIFUNCTIONAL GASOLINE ADDITIVES]

22 Dated filed .... 10 September 1970, at 10:30 hrs.
Date of the decisions to issue .... 4 April 1972
Publication of the granting .... B.O.P.I. - "Listes" no. 17 of 28 April 1972.

51 International classification (Int. Cl.) C 07 c 93/00//C 07 f 9/00; C 10 1 1/00.

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54 New nitrogenated additives with multifunctional usage for fuels.

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33 32 31 Conventional Priority:

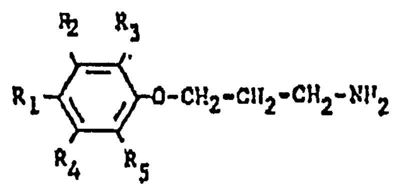
This invention relates to improved additives containing nitrogen, intended for fuel compositions that can be used in spark-ignition engines. The use of fuels based on gasoline, especially for automobile engines, results in several problems in the carburetor area.

The first problem is the problem of the considerable formation of deposits on the different elements of the carburetor, deposits which are responsible for failure and stalling of the engine. These types of disadvantages are frequently encountered in automobile engines, especially in dense city traffic and in hot weather. Furthermore, the development of the positive crankcase ventilation device (PCV), whose purpose is to reduce atmospheric pollution, also contributes considerably to the formation of this type of deposits. The second problem relates to the appearance of ice crystals, which adhere to the metal walls of the carburetor when certain atmospheric conditions are present involving the degree of humidity of the air and its temperature. The accumulation of these ice crystals can be sufficiently great to clog the intake orifice in the area of the throttle valve of the carburetor. The third problem consists of corrosion of the metal parts of the engine by water dissolved in the gasoline. These three problems can be eliminated by using additives dissolved in the gasoline even at very low concentrations on the order of 50 parts per million (ppm) by weight. These additives have a detergent effect, which eliminates deposits formed in the carburetor, a surfactive effect which avoids the adhesion of ice crystals to the metal walls, and finally an anticorrosion effect due to the development of a protective film on the different metal parts of the engine. More precisely, the origin of the combined effects of this type of additive for gasolines appears to be due to the chemical nature of these substances, which comprise an aliphatic part soluble in gasoline and one or more polar parts responsible for these different effects. Furthermore, it is interesting, mainly for economic reasons, to try to combine the above-cited effects in one single molecule. Chemical structures of this type are achieved with the compounds which are the objects of the present invention and give a fuel mixture containing them the various effects that have been described, namely, detergency, an antifreeze effect, and an anticorrosion effect.

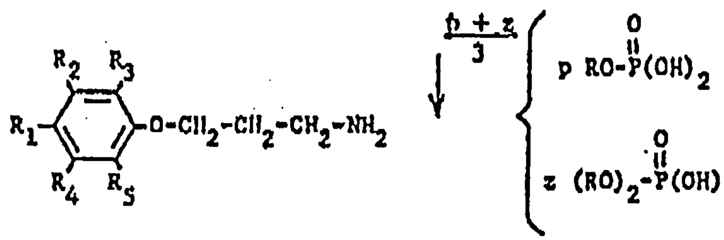
On the other hand, it has been observed that the increase in polar groups obtained by the combination of compounds of the alkylphosphoric acid type on nitrogenated compounds increased considerably the solubility of the additive in aromatic solvent mixtures and strengthened some of the above-cited effects, in particular the antifreeze effect.

The object of the invention is achieved by using at least one compound represented by one of the following formulas:

I



II



In formula I, R_1 R_2 R_3 R_4 R_5 are selected from the group comprising hydrogen and the straight or branched hydrocarbon radicals, and the total number of carbon atoms in R_1 R_2 R_3 R_4 R_5 taken together varies from 0 to 30. In formula II, R_1 R_2 R_3 R_4 have the same meaning as above, R represents a straight or branched aliphatic hydrocarbon radical whose number of carbon atoms may vary from 8 to 18; p and z are integers selected so that the sum of the OH functions involved neutralize the amine function of the compound represented by formula I.

The compounds according to formula I are obtained by using the product of cyanoethylation of an alkylphenol or one of its derivatives with the acrylonitrile itself or a mixture of acrylonitrile and an aromatic solvent such as benzene, for example, while making sure that the acrylonitrile is always in great excess with respect to the alkylphenol used. The catalyst that one will use shall be a basic agent such as alcoholic potassium hydroxide or a quaternary ammonium hydroxide, for example, triton B. The cyanoethylation reaction is carried out under reflux of the reagents for several hours. At the end of the reaction the mixture is taken up with ether and filtered in order to eliminate the polyacrylonitrile which has been able to form, and the mixture is then evaporated. One then obtains an oil which one dissolves in an alcohol with a low molecular weight such as methanol or ethanol, saturates with ammonia and adds a hydrogenation catalyst, for example, nickel or cobalt. The mixture thus obtained is hydrogenated in an autoclave under a pressure close to 150 kg/cm^2 at a temperature on the order of 120°C for approximately 5 h. After filtration of the reaction mixture obtained at the

end of the hydrogenation, one evaporates the alcohol and obtains an oil which one places in solution in an aromatic solvent such as toluene or benzene.

The aromatic solution of the compound according to formula I thus obtained is titrated according to classical methods: volumetric titration, which makes it possible to determine the amine value of this solution and use it for the above-cited industrial uses.

The compound according to formula II can be obtained from the action of an alkylphosphoric acid or a mixture thereof on a compound such as I.

Among the alkylphosphoric acids that can be used, the mixture of mono- and di-alkylphosphoric acids obtained from the action of phosphoric anhydride on a mixture of straight or branched aliphatic alcohols of the "oxo" alcohol type is particularly advantageous.

The action can be represented by the following equation:

$$3\ R'OH + P_2O_5 \longrightarrow (R'O)_2\ POOH + (R'O)-\overset{\overset{\displaystyle O}{\|}}{P}-(OH)_2$$

R' designates a straight or branched alkyl radical whose number of carbon atoms varies from 8 to 18. The choice of the alcohol used can be guided by the desire to obtain a fuel composition resistant to aqueous extraction. The use of branched alcohols of the ethylhexyl type, for example, is recommended for this purpose.

The neutralization reaction can be carried out by the addition of the selected acid to a solution of compound I in an aromatic solvent while keeping the reaction mixture at a moderate temperature for several hours. At the end of the reaction, one obtains an oil that can be used for the industrial usages already cited.

The compounds that are the objects of the invention can be used in gasolines at concentrations that may vary between 10 and 100 ppm by weight, without the formation of turbidity in the fuel even at low temperature, and combined with other commercial additives without any disadvantage.

The objects of the invention will be understood better from the nonlimiting examples that follow.

Example I

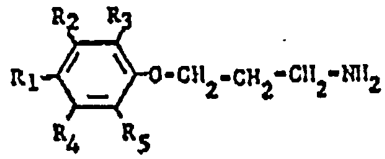
In a 500-mL, three-necked flask equipped with a reflux condenser, a thermometer and bubbling of argon, one places 44.08 g nonylphenol or 0.2 mole, 127.34 g acrylonitrile or 2.4 mole and 3 mL triton B. The reaction mixture is brought to reflux for 24 h, and then the solution is taken up in ether, filtered and washed with water. The ether phase is dried over magnesium sulfate and then evaporated. One obtains an oil (56.53 g), whose analysis and I.R. spectrum show that it involves a compound containing the nitrile and ether groups resulting from the cyanoethylation of the nonylphenol. The yield of the reaction is 70%. 26 g of the oil thus obtained is dissolved in 105 mL of methanol in which one has previously dissolved 10.95 g ammonia. To the mixture one adds 3 g Raney nickel, and the entire mixture is placed in a 250-mL autoclave. The hydrogen pressure is brought to 150 kg/cm^2, and the temperature is raised to 120°C for three h and then kept for an additional 2 h at this temperature while stirring the apparatus continuously. One filters the methanol solution at the end of the reaction, and then one evaporates the solvent. One then obtains 25.26 g of oil whose infrared analysis shows that it involves a compound described by formula I, where R_1 = nonyl and $R_2 = R_3 = R_4 = R_5 = H$. The yield of the hydrogenation reaction is determined by titrating the amine groups volumetrically with a previously titrated perchloric acid. The hydrogenation yield is 90.5% with respect to the nitrile involved. The yield of compound I is then 64% with respect to the alkylphenol initially used.

Example II

In a three-necked flask equipped with a thermometer, a stirrer and an introduction device, one places 48.32 g of a sulfuric solution of a previously titrated compound I. One then adds over 1/2 h 13.8 g of an equimolar mixture of monoacidic and diacidic octylphosphoric acid. One then keeps stirring for 1 h 30 min at a temperature of approximately 70°C. At the end of the reaction one has a titrated xylene solution of the compound described by formula II, where R_1 = nonyl, $R_2 = R_3 = R_4 = R_5 = H$, R = octyl, p = z = 1.

Claims

1. New organic compounds according to the formula:



in which R_1, R_2, R_3, R_4, and R_5 are selected from the group consisting of hydrogen and the monovalent hydrocarbon radicals containing from 1 to 30 carbon atoms.

2. New organic compounds according to claim 1, furthermore comprising at least one molecule selected from the alkylphosphoric acids of the formulas

$$RO-\overset{O}{\overset{\|}{P}}(OH)_2 \quad \text{and} \quad (RO)_2\overset{O}{\overset{\|}{P}}-OH$$

in which R is a saturated monovalent aliphatic hydrocarbon radical which comprises from 8 to 18 carbon atoms, the number of alkylphosphoric acid molecules being such that the number of OH groups is at the most equal to the number of amine groups.

3. Process for preparation of a compound according to claim 1, in which one reacts an alkylphenol with acrylonitrile followed by hydrogenation of the compound obtained.

4. Process of preparation of a compound according to claim 2, in which one adds to a compound according to claim 1 at least one alkylphosphoric acid prepared by the action of phosphoric anhydride on at least one straight or branched aliphatic alcohol whose molecule comprises from 8 to 18 carbon atoms.

5. The use of products according to claims 1 and 2 as additives to gasolines with detergent, antifreeze and anticorrosion effect.

6. The use according to claim 5, in which one uses an additive concentration lying between 10 and 100 parts per million by weight.

7. The gasolines comprising at least one compound according to one of claims 1 and 2.